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Generalised coexistence of a low work function and a stable surface: $CaAl_4$ and $BaAuIn_3$

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Abstract

Cathodes are used in many devices ranging from microwave ovens to organic light-emitting diodes (OLEDs). Crucial materials properties are a low work function (Φ) and a (relatively) stable surface. The relation between the two was not clear for more-complex metals. Our previous paper [M.A. Uijttewaal, G.A. de Wijs, R.A. de Groot, R. Coehoorn, V. van Elsbergen, C.H.L. Weijtens, Chem. Mater. 17 (2005) 3879] predicted, on the basis of results on $BaAl_4$, that stable low-work-function surfaces are more general for intermetallic compounds with polar surfaces. This paper strengthens the prediction by first-principles calculations on various surfaces of $CaAl_4$ and $BaAuIn_3$.

Keywords: Work function; Ab initio; Density functional calculations; Anisotropy; Relaxation; Stability; Compound; Surfaces

1. Introduction

Electron-emitting materials are increasingly applied in technology. It is therefore all the more important to understand how the work function (Φ) and the stability[1] of a cathode metal are related. Two examples of technology incorporating cathodes are vacuum electronic devices such as cathode-ray tubes (CRTs) and organic light-emitting diodes (OLEDs). In CRTs, a thin layer of a low-Φ metal is often present on top of a cathode made from a structurally stable material to enhance its electron-emitting properties [1]. Electron injection into OLEDs strongly depends on the cathode work function [2]. The lifetime of the device, on the other hand, derives from a subtle interplay between high voltages and reaction of the cathode with the organic material. OLEDs with single-element cathodes can be greatly improved, in terms of lifetime and luminosity, by first evaporating a small layer of a low-Φ metal on the polymer [3a-b] . Thus the relationship between Φ and (surface) stability is crucial. It is, however, poorly understood, especially for more-complex metals.

The general rule for elements is that a low work function and high (surface) stability are incompatible: the element with the lowest work function, cesium ($\Phi = 2.14$ eV [4]), is highly reactive and has a low melting temperature. Noble metals (silver/gold/platinum) on the other hand are hardest to oxidize, but their Φ is at least twice as large (4.25/5.1/5.65 eV [4]). The general viewpoint is that a low Φ always implies loosely bound electrons that easily mediate reactions. Another aspect is the surface anisotropy of the work function, which can be quite large. For tungsten, e.g., it is of the order of 1 eV [5]. The model of Smoluchowski [6] explains well that a surface with a decreased Φ is destabilized. These surfaces namely contain a larger area per surface atom and therefore more broken bonds. The combined observations make one believe that stable, low-work-function surfaces are not possible for more-complex metals either.

In contrast, previous work [7] showed that the surface with the lowest work function is also the most stable one,

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[1] The concept of stability is discussed in Section 4.

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at least for $BaAl_4$. From analysis of the results we predicted that this should be a more general feature of complex metals, more specifically of intermetallic compounds with polar unit cells. The electronegativity difference of the constituting elements of the compound improves both work function and stability of the cationic surface. In this paper, the validity of the prediction is clarified by ab initio calculating the structural relaxation, work functions and surface energies of various surfaces of the intermetallic compounds $CaAl_4$ and $BaAuIn_3$.

2. Ab initio calculations

The first-principles calculations were carried out using density functional theory (DFT) in the local density approximation (LDA [8a-b]) with generalised gradient corrections (GGA [9]). We used the total energy and molecular dynamics program VASP (Vienna ab initio Simulation Package [10a–c]), which has the projector-augmented-wave method (PAW [11a-b]) implemented. Nonlinear core corrections [12] were applied for all atoms. A semi-core of Ba 5s and 5p electrons was included as well as 4d electrons for In. The Kohn-Sham orbitals were expanded in plane waves with kinetic energy cutoffs of 18 Ry. The Brillouin zones for the calculations of the tetragonal $BaAuIn_3$ surfaces (see below) were sampled with $1 \cdot 4 \cdot 6$ (100) and $8 \cdot 8 \cdot 1$ (001) Monkhorst–Pack [13] k point grids, resulting in 12 and 25 k points, respectively, in their irreducible parts. The (periodically repeated) unit cells contained slabs with thicknesses of six bulk unit cells and at least 11 Å vacuum. The Brillouin zones for the calculations of monoclinic $CaAl_4$ surfaces (see below) were sampled with $1 \cdot 8 \cdot 8$ (010), $1 \cdot 8 \cdot 6$ (ab) and at least $8 \cdot 8 \cdot 1$ {various (001)} Monkhorst–Pack k point grids, resulting in 34, 26 and at least 36 k points, respectively, in their irreducible parts. Except for (001)Al, their unit cells contained slabs with thicknesses of minimally six bulk unit cells and at least 11 Å vacuum.

The crystal structures of $CaAl_4$ [14] and $BaAuIn_3$ [15] are depicted in Figs. 1 and 2. Both are based on the $BaAl_4$ structure [16], a very frequently occuring crystal structure. It is body-centered tetragonal, with alternately three aluminum layers and one barium layer in the [001] direction. The $CaAl_4$ structure has a small monoclinic distortion below 170 °C caused by the smallness of Ca atoms with respect to the surrounding Al cages. Experimentally determined lattice constants are $a = 6.153$ Å, $b = 6.173$ Å, $\beta = 118.15°$ and $c = 6.329$ Å. Our theoretical values deviate less than 0.6%. The lattice parameters of the $CaAl_4$ structure are about 5% smaller than that of $BaAl_4$, not unexpected since the atomic radius of Ca is 10% smaller than that of Ba. The binding energy per formula unit (F.U.) is calculated at 1.19 eV with respect to the elemental metals Ca and Al. It compares favourably with the

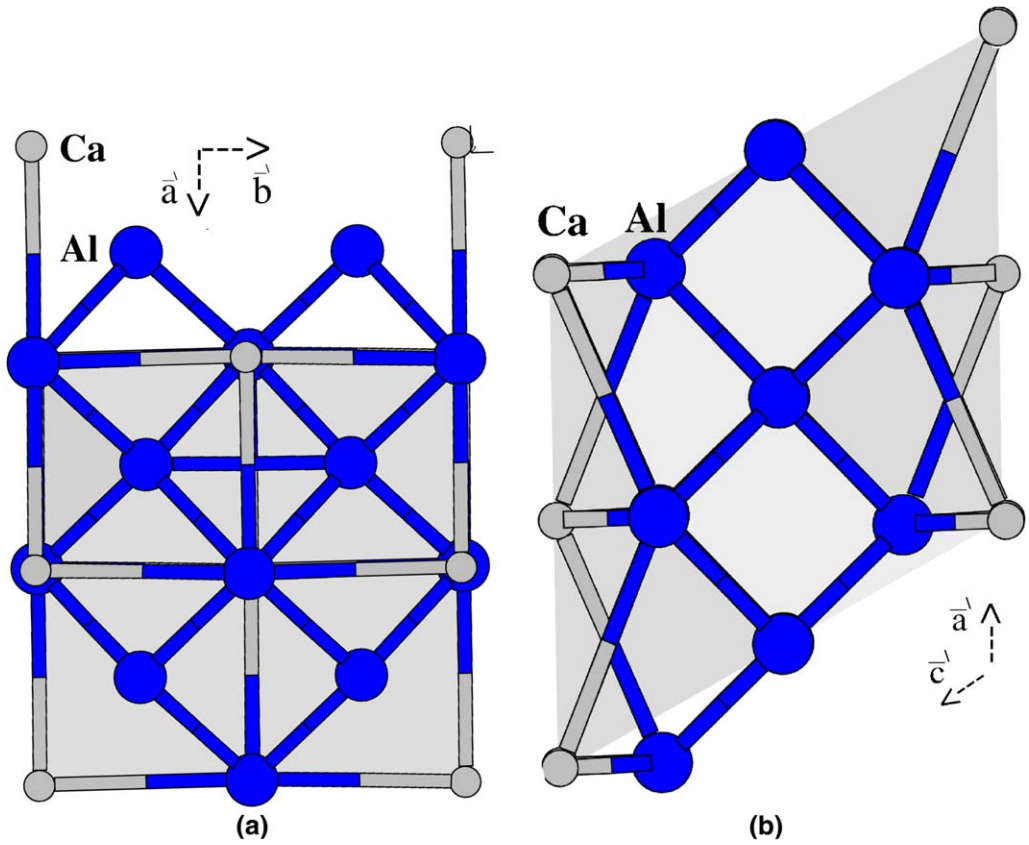

Fig. 1. Top and side view of the monoclinically distorted body centered tetragonal unit cell of $CaAl_4$ containing two formula units.

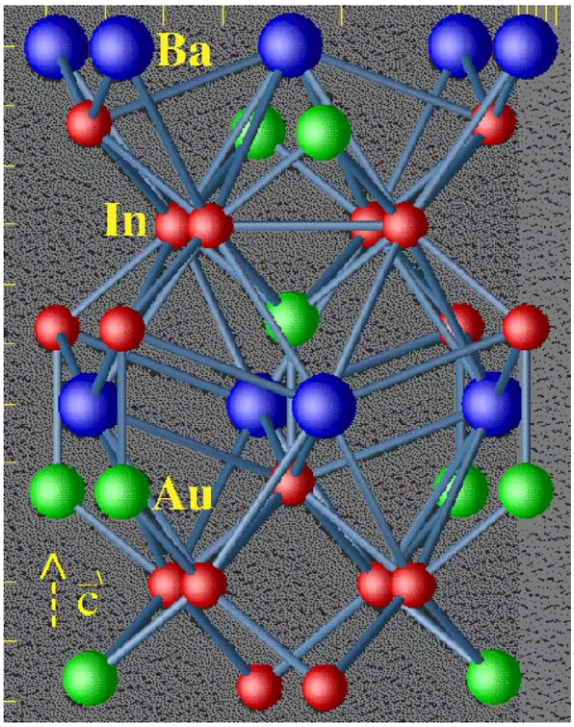

Fig. 2. BCT unit cell of $BaAuIn_3$ containing 4 F.U. and showing the modeled disorder in Au positions.

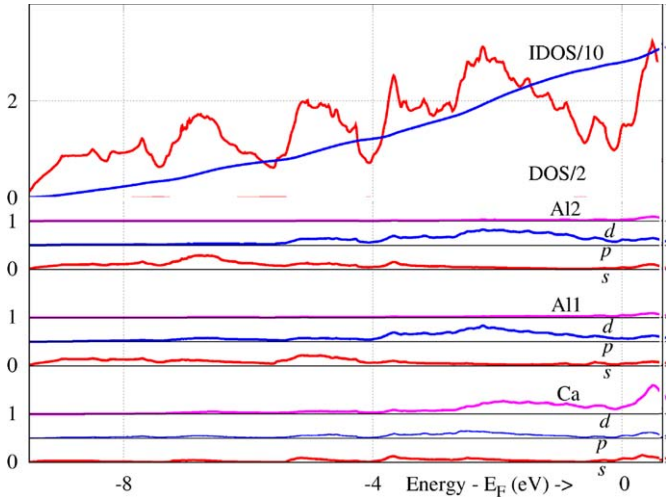

Fig. 3. Density of states (states/eV) of $CaAl_4$. Integrated DOS and partial DOS of crystallographic nonequivalent atoms are also plotted. Al1 atoms neighbour calciums. The radii used for the atoms are 2.0 Å (Ca) and 1.43 Å (Al).

experimental enthalpy of formation at 527 °C of 1.04 eV [17] and is somewhat less than the (calculated) binding energy of $BaAl_4$ (1.42 eV/F.U.). The calculated binding energy of $BaAuIn_3$ is 2.61 eV/F.U. There is no experimental report to compare with, unfortunately, but it is quite larger than that of $BaAl_4$. In the $BaAuIn_3$ structure gold randomly substitutes for In in layers neighbouring Ba. It is modeled by placing the Au atoms on next-nearest-neighbouring sites. The unit cell then contains 2 F.U. Calculated lattice constants for $BaAuIn_3$ are $a = 6.86$ Å, $b = 6.83$ Å and $c = 12.08$ Å. These differ less than 1% from those determined experimentally. $BaAuIn_3$ is about 8% larger than $BaAl_4$ following the 17% larger atomic radius of In with respect to that of Al.

Various surfaces can be constructed from the depicted bulk unit cells. Already four different surface terminations are possible in the [0 0 1] direction of both compounds: surfaces only consisting of Ba or Ca, aluminum surfaces ending with one, two or three Al layers (Al1, Al2, Al3) for $CaAl_4$, and for $BaAuIn_3$ a pure In surface (In2) and two mixed Au/In surfaces (AuIn1 and AuIn3). Only one surface is possible in the [1 0 0] direction of $BaAuIn_3$, which nessesarily is stoichiometric. In the case of $CaAl_4$ the stoichiometric surface is the one normal to the $[a + b]$ direction. We call it (*ab*). The $CaAl_4$ (0 1 0) surface containing Ca is also considered in this study as well as (0 0 1) surfaces whose calciums are substituted by Sr or Ba.

The bulk density of states (DOS) of $CaAl_4$ has a quasi gap just below the Fermi level as shown in Fig. 3. This is common for the $BaAl_4$ structure [16]. It compares very well with the DFT pseudopotential calculation from Ref. [16]. It strongly differs, however, from the extended Hückel tight-binding result in Ref. [14]. From the plotted partial DOS it can be seen that calcium is all but deprived of its s electrons, which suggests charge transfer to aluminum. The density of states at the Fermi level is mainly a combination of Ca d states and Al p states. The DOS of $BaAuIn_3$ (Fig. 4) shows a quasi-gap about 1 eV above the Fermi level. The density at the Fermi level mainly consists of Ba d states and In p states. These results differ strongly from the extended Hückel tight-binding calculation in Ref. [15]. We cannot tell whether this merely reflects the increased accuracy of the method or signifies differences in the modelling of Au positional disorder.

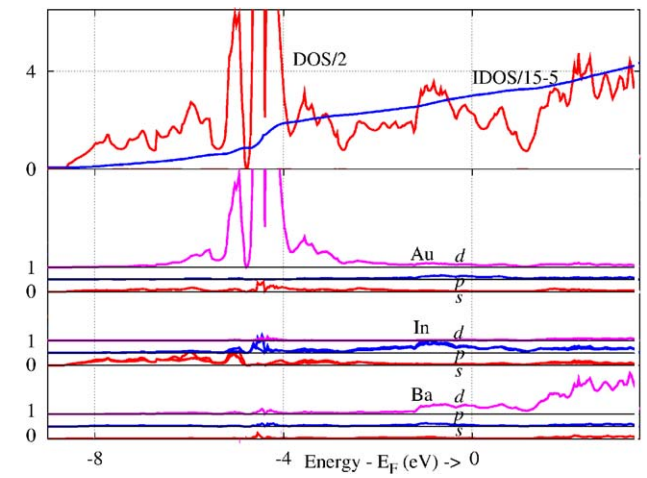

Fig. 4. The density of states (states/eV) of $BaAuIn_3$. The integrated and partial DOS of the 3 atomic species are also plotted. The radii used for the atoms are 2.2 Å (Ba), 1.44 Å (Au) and 1.67 Å (In).

3. Work function

The work function is defined as the amount of energy it takes to extract electrons from a metal, i.e., bring them from the Fermi level (E_F) to the vacuum V_{vac}.

$$\Phi = V_{vac} - E_F$$

At locations that are microscopically far from the material, but macroscopically near it, Φ is surface dependent. The work function at large distance is then an average over the various surfaces [18].

The method to calculate the work function of a specific surface is described in Ref. [7]. A bulk calculation provides an accurate E_F. Then by means of the average potential in a bulk unit cell ($\langle V \rangle_{bulk}$) the Fermi level can be compared with the vacuum potential of a calculation with a slab of material. Accuracies better than a tenth of an eV can be achieved with moderate slab widths [19].

Figs. 5 and 6 display the work functions of the various $CaAl_4$ and $BaAuIn_3$ surfaces, respectively. Experimental (polycrystalline) Φ values of the different elements are shown at the figure borders for comparison. Those for Ba (2.32 eV), Ca (2.87 eV) and Al {4.41 eV (100) and 4.24 eV (111) [4]} compare favourably with our calculated work functions of bcc-barium [2.36 eV (100) and 2.27 eV (111)], fcc-calcium [2.81 eV (100) and 3.08 eV (111)] and fcc-aluminum [4.34 eV (100) and 4.17 eV (111)]. No experimental work functions of $CaAl_4$ and $BaAuIn_3$ are available to compare with the calculated results.

Structural relaxation of the $BaAuIn_3$ (100) surface makes the surface indium atoms move outward by about .2 Å while both barium and gold move inward, Ba by less than .1 Å and Au by about .15 Å. As a consequence the (100) work function increases 0.16 eV. On the other hand the Φ's of the (001)Ba and (001)AuIn3 surfaces are somewhat lowered by relaxation. The Ba surface atoms have moved inward by nearly .2 Å while the neighbouring Au and In have moved outward by .2 Å, respectively .25 Å. The resulting Φ for (001)Ba is 2.00 eV, quite lower than the elemental work function of barium. The $CaAl_4$ work functions of both the (010) and the (*ab*) surface increase during relaxation of the structure. The (010) surface starts out lower (it contains more Ca) and increases more (the surface density of atoms is lower). The calciums of the (001) Ca surface move .4 Å in during relaxation while the neighbouring aluminums move .2 Å out. This increases the work function by 0.3 eV. Still, it is 0.3 eV below the elemental value of Ca.

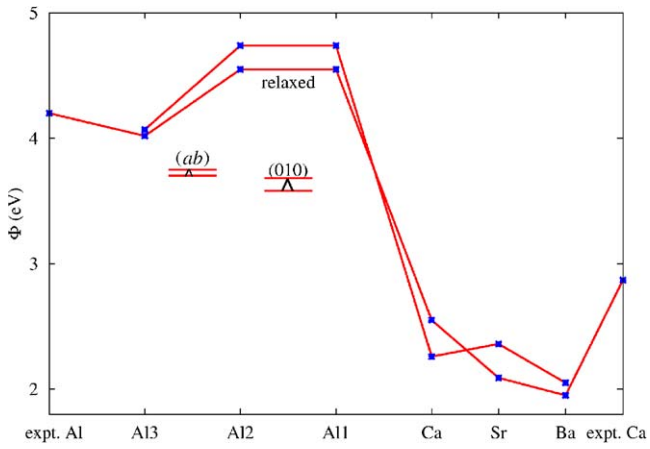

Fig. 5. Work functions (eV) of the $CaAl_4$ (001) surfaces both before and after structural relaxation. Names of the surfaces are explained in the text. Sr and Ba indicate (001)Ca surfaces of which the surface calciums are replaced by strontium and barium atoms, respectively. Structural relaxation of Sr starts at the relaxed Ca positions and that of Ba at the unrelaxed ones. Experimental polycrystalline values for calcium and aluminum are indicated at the borders. Lines connect the data points. Φ's for the (010) and (*ab*) surfaces before and after relaxation are inserted.

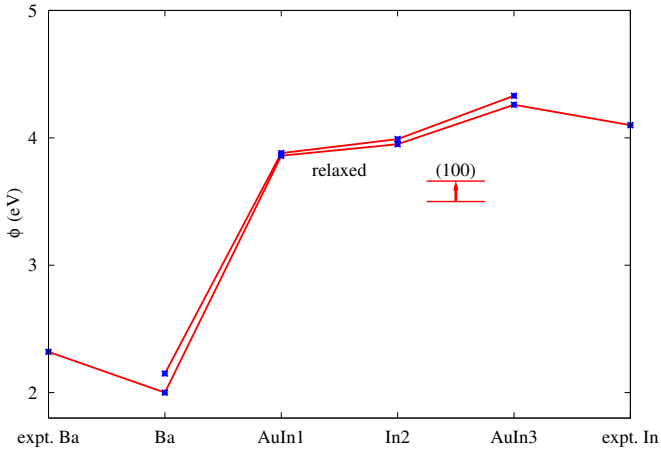

Fig. 6. Work functions (eV) of the $BaAuIn_3$ (001) surfaces both before and after structural relaxation. Names of the surfaces are explained in the text. Experimental polycrystalline values for barium and indium are indicated at the borders. Lines connect the data points. Φ's for the (100) surface before and after relaxation are inserted.

It is interesting to consider what happens when we replace calcium atoms of the (001)Ca surface with Sr or Ba. Fig. 5 reveals that these modifications have a favourable influence on the work function. Two atomic properties are responsible for this. In the first place Ba and Sr are more electropositive than Ca which causes a larger charge transfer to the anions. Secondly the surface filling has increased as the atomic radii of Ba and Sr are larger than that of Ca. Therefore the Al contribution to the work function has decreased. Structural relaxation enhances Φ further. For the Sr surface it reduces the displacements of (001)Ca by a factor of 2. Relaxation of the Ba surface is started at the original (bulk) positions and hardly displaces barium atoms inward while neighbouring aluminums move .1 Å outward. The new minimum value of the work function (1.95 eV for Ba substitution) is equal to the (001)Ba surface of $BaAl_4$.

Concluding this section we can say that at least low work functions are not confined to $BaAl_4$. Moreover surface atom modifications can even improve them.

4. Surface stability

The stability of a surface is a complex notion. It not only depends on the (initial) surface energy (γ), but also on the energy of the final or transition state one considers. Hence several types of stability exist: towards decomposition, deformation, roughening, chemical reactions, *etcetera*. The binding energy of a compound estimates its stability towards decomposition. The anisotropy in surface energy determines the deformation stability. The energy of the roughened surface, on the other hand, contains contributions from surfaces of other indices. These will differ little for (elemental) cubic systems, but not so for layered compounds. In any case, lowering the energy of the surface under consideration increases its stability indiscriminately. The energy of a surface will therefore be taken as the measure of its stability.

How γ is calculated is described in Ref. [7]. It is the difference between the energy of a slab and the equivalent bulk, normalised to unit area. Non-stoichiometric slabs do not have an equivalent bulk and thus the energies of their surfaces vary with Ca or Ba chemical potential. Those range from their elemental bulk value to that minus the binding energy of the compound under consideration. Chemical potentials can be controlled during crystallization. In general, surfaces of different index are formed with surface areas inversely proportional to their energies [20]. Only the most stable one will be formed, however, of different surface terminations with the same index.

The surface energies of $CaAl_4$ and $BaAuIn_3$ are drawn in Figs. 7 and 8, respectively. They cannot be compared to experiments because of lack of data. For all surfaces the decrease in energy with relaxation is plotted. (001)dip indicates the energy of a (001)$BaAuIn_3$ slab with one Ba surface and one AuIn3 surface. It is the average of their γ's. The green line named AuIn1/In2 is also an average, namely of γ's of (001)AuIn1 and (001)In2 surfaces. These cannot be split up since the third atomic species in $BaAuIn_3$ introduces an extra degree of freedom and thus an uncertainty in the surface energies. This is largest at the barium bulk chemical potential. Only the combination AuIn1/In2 has a unique γ. No single surface is the most stable contrary to the case of $BaAl_4$. Still the (001)Ba surface of $BaAuIn_3$ is significantly lower in energy than the other ones in most part of the plot. For the compound $CaAl_4$, the (001)Al1 and (001)Al2 surface are averaged for simplicity. The (010) surface is a little higher in energy than the (*ab*) surface in accordance with traditional arguments for a surface with a decreased Φ. On the other hand, the relaxed (001)Ca surface is the most stable one in the entire range of chemical potentials although its work function is much lower than that of either the (010) or the (*ab*) surface. It nicely confirm the prediction that for a polar intermetallic compound like $CaAl_4$, the lowest-work-function surface is also the most stable.

Let's again consider (001)$CaAl_4$ surfaces ending with an additional monolayer Ba or Sr. Their surface energies are governed by an extra free parameter namely the chemical potential of the surface adatoms. By fixing the potentials at their elemental bulk values, the energies of these surfaces can be compared with the γ's of $CaAl_4$ surfaces. The Ba surface then becomes the most stable one followed by the Sr surface. Their energies are .34 eV/nm^2, respectively .95 eV/nm^2 at the chemical potential of calcium bulk. In most part of the plot they are even negative, which means that $CaAl_4$ with a barium or strontium surface is favoured over bulk $CaAl_4$ and elemental bulk Ba or Sr. The unusual

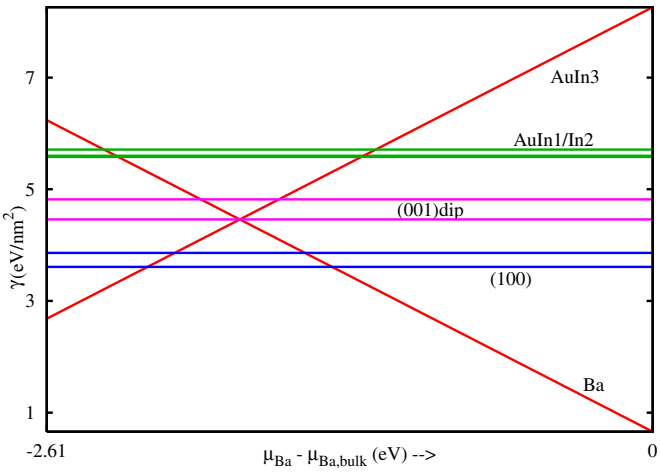

Fig. 8. Surface energies (eV/nm^2) for the $BaAuIn_3$ surfaces as function of the barium chemical potential (eV). The potential ranges from the potential of Ba bulk to that minus the binding energy of $BaAuIn_3$. Surface names are explained in the text. The effect of relaxation is indicated for each surface. The energies of the AuIn1 and In2 surface are averaged. The (001)Ba surface is the most stable in the largest part of the plot.

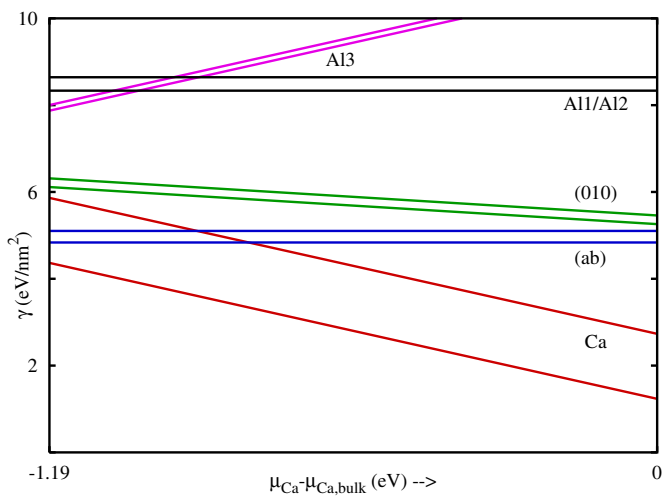

Fig. 7. Surface energies (eV/nm^2) for the $CaAl_4$ surfaces as function of the calcium chemical potential (eV). The potential ranges from the potential of Ca bulk to that minus the binding energy of $CaAl_4$. Surface names are explained in the text. The effect of relaxation is indicated for each surface. The energies of the Al1 and Al2 surfaces are averaged for simplicity. The (001)Ca surface is the most stable in the entire plot.

stability of the Ba and Sr surfaces is explained by noticing that $BaAl_4$ and $SrAl_4$ both are more stable than $CaAl_4$. Therefore Ba–Al and Sr–Al bonds must be stronger than Ca–Al bonds.

5. Conclusions

To summarize, we used first-principles calculations on various surfaces of $CaAl_4$ and $BaAuIn_3$ to further clarify the relation between work function and surface energy in more-complex metals. The binding energies of these compounds are 1.19 eV/F.U. and 2.61 eV/F.U., respectively, and these compare favourably with available experimental results. As in our previous study ([7]) the most stable surfaces {Ca and Ba terminated (0 0 1) for $CaAl_4$ and $BaAuIn_3$, respectively} have the lowest Φ of the compound surfaces considered. These are significantly lower than the elemental Φ values of Ca and Ba even when full structural relaxation is taken into account. Moreover, in the case of $CaAl_4$ results can be improved by replacing surface calciums with barium or strontium. Then both work function and surface energy are reduced further.

These results strengthen the prediction that stable, low-Φ surfaces are generic in intermetallic compounds with polar unit cells. They also point the direction for improvement of cathodes in e.g., OLEDs.

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